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(54) Title: PROCESS AND APPARATUS FOR PREPARING HETEROGENEOUS CATALYSTS		
(57) Abstract		
<p>The invention relates to a process and to an apparatus for preparing a heterogeneous catalyst having at least one catalytically active species bound to the surface of a support material. According to the process, the surface of the support (6) is first pretreated. A catalyst reagent containing the catalytically active species or its precursor is vapourised and the vapour is routed into a reaction chamber (6) where it is brought to interact with the support material. The catalyst reagent not bound to the support is withdrawn from the reaction chamber (4) in gaseous form. If necessary, the species bound to the support is post-treated in order to convert it into a catalytically active form. According to the invention, the amount of catalyst reagent brought into the reaction chamber is at least equal to, preferably in excess of the number of available binding sites on the surface (6). The temperature of the support is kept higher than the condensation temperature of the vapour and at the same time at a sufficiently high level to attain the thermal activation energy needed for forming bonds between the active species and the support. By binding the catalytically active species in this way to the support, it is possible to provide a heterogeneous catalyst having a high activity even at small amounts of the active species.</p>		

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Process and apparatus for preparing heterogeneous catalysts

The present invention relates to a process according to the preamble of claim 1, for preparing a heterogeneous catalyst comprising a support and at least one catalytically active species bound to its surface.

According to such a process, the surface of the support is optionally first pretreated. The catalyst reagent containing the catalytically active species or its precursor is vaporized and the vapour is conducted to a reaction chamber where it is contacted with the support. The catalyst reagent not bound to the support is then withdrawn in gaseous form from the reaction chamber. If necessary, the species bound to the support is posttreated in order to convert it into a catalytically active form.

The invention also relates to an apparatus according to the preamble of claim 15, for preparing heterogeneous catalysts.

As far as the prior art is concerned, reference is made to the following publications:

1. GB Patent Specification No. 1,105,564 (1968)
2. US Patent Specification No. 4,262,102 (1981)
3. US Patent Specification No. 4,362,654 (1982)
4. US Patent Specification No. 4,380,616 (1983)
5. Kase, A., Asakura, K., Egawa, C. and Iwasawa, Y., New Pd/Ultra-Thin Amorphous-Oxide Layer/ZSM-5 Catalysts for Selective Formation of Propane from CO/H₂, Chem. Lett. 6 (1986) 855-858
6. Asakura, K. and Iwasawa, Y., The Surface Structure and Catalytic Properties of One Atomic Layer Amorphous Niobium Oxide Attached on Silicon Dioxide, Chem. Lett. 6 (1986) 859-862

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 8. Asakura, K, Aoki., M. and Iwasawa, Y, Selective Isopentane Formation from CH₃OH on a New One Atomic Layer ZrO₂/ZSM-5' Hybrid Catalyst, Catalysis Lett. 1(1988), 395-404
 10. McDaniel, M.P., The State of Cr(VI) on the Phillips Polymersation Catalyst II: The Reaction between Silica and CrO₂Cl₂, Journal of Catalysis 76 (1982) 17-28
 15. US Patent Specification No. 4,439,543 (1984)
- 15 Traditionally, heterogeneous catalysts have been prepared by depositing catalytically active compounds from the liquid phase onto the surface of the support by means of impregnation, precipitation or ion exchange. The starting materials used here comprise chemical compounds, often salts, which are soluble in known solvents. The solvents most frequently employed are water and different alcohols.
- 20 One drawback of the conventional technology is the large number of stages involved in catalyst preparation. The preparation of catalysts is recognised as an extremely delicate procedure requiring very accurate control of each requisite stage of the process.
- 25 Another drawback of prior art methods is associated with the need for solvents. The solvents by themselves often react with the support causing changes to the surface structure. This is particularly the case with the use of zeolites as the support material. The acidity of the surface has a decisive effect on the activity of the catalyst. The acidity is influenced both by the type of the acid sites, for example, the Brönstedt and Lewis type, as well as by the number of sites. The acid sites can be influenced by, e.g., different heat treatments. When zeolites are treated with
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solvents, especially water, after a heat treatment, a definite change in the distribution of the acid sites is discernible. At least some of the acid sites then assume reversibly different forms. Thus, it is clear that the degree of acidity cannot be controlled during impregnation or ion exchange.

In addition to the above-mentioned drawbacks, the solvents used are often contaminated with impurities that can adversely affect the activity of the catalyst.

- 10 In order to eliminate the cited drawbacks of the liquid phase preparation processes, a number of different gas phase processes have been developed.
- 15 Reference [1] outlines a process that involves heating rhenium heptoxide to a temperature in the range from 150° to 700°C and allowing the vapour to condense on the surface of an aluminium oxide support which is maintained at a temperature below 50°C. Alternatively, the reaction is carried out at a temperature between 500° and 600°C, the Re₂O₇ partially decomposing to rhenium metal and forming a metal deposition on the alumina. The citation includes an example disclosing the preparation of a catalyst containing 14 % Re₂O₇.
- 20 25 In the following three references [2, 3 and 4], processes for preparing silica-supported chromium catalysts have been described. The US Patent Specification No. 4,262,102 presents a method that involves vaporizing elemental chromium by heating it to a temperature of from 1400° to 1700°C in a high vacuum metal evaporator, the chromium sublimating from the vapour phase on a chilled support in the form of small particles [2]. The procedures described in US Patent Specifications Nos. 4,362,654 and 4,380,616 comprise placing the silica support and a piece of chromium metal in a round-bottomed flask, evacuating the flask, and stirring the silica in the flask with a magnetic stirrer. The chromium is

vaporized by heating with heat resistances [3 and 4]. In this case also, the chromium adheres to the support surface in the form of small particles.

- 5 In processes of the above type, the dispersion of the active metal may be heterogenic and there is not yet a proper understanding of how the carbene complex is formed on the catalyst.
- 10 In the Department of Chemistry at Tokyo University, researchers have prepared different catalysts having extremely thin layers, known as "atomic layers", of metal oxide bound to the surface of the supports [5 - 8]. Ideally, the catalysts comprises 1 to 3 of these atomic layers.
- 15 Reference [5] discloses the preparation of catalysts having ultra-thin La_2O_3 , TiO_2 , SiO_2 , and Nb_2O_5 layers on the outer surface of a zeolite (ZSM-5). Reference [6] describes the corresponding catalysts having a SiO_2 support. According to reference [5], catalysts containing SiO_2 and TiO_2 are prepared by contacting methyltriethoxysilane and titanium isopropoxide vapors with the hydroxyls of ZSM-5 surfaces at 473 K (200°C) in a vacuum. Similarly, the $\text{ZrO}_2/\text{ZSM-5}$ hybrid catalyst was prepared by contacting vaporized zr tetroxide having a vapour pressure of 133 Pa at 473 K with ZSM-5 at the same temperature. By repeating the binding reaction about 3 times, in both cases a single atom oxide layer covering the whole surface of the support was obtained.
- 20 According to the authors of the cited articles, the catalysts thus prepared have unique properties. In particular, the catalysts exhibit good selectivity. Thus, the catalysts prepared according to reference [5] are used for selective propane preparation from CO and H_2 . The catalyst described in reference [6] is used during ethanol dehydrogenation, this catalyst being more active and selective than a catalyst prepared by impregnation or Nb_2O_5 . The catalyst cited in reference [8] activates the formation of isopentane from methanol.

The common feature of the methods cited in references [5] to [8] is that first, a thin oxide layer is prepared on the surface of the support. The starting metal compound is chosen such that it does not fit into the cavities of the
5 zeolite [5, 8].

McDaniel has studied the state of chromium(VI) on a Phillips polymerisation catalyst [9] and he has also, together with Stricklen, patented a process for preparing a CO-reduced chromyl halide silica-supported catalyst [10]. The starting compounds chosen include CrO_2Cl_2 , CrO_2F_2 and CrO_2FCl . Before depositing the starting compound on the support, the surface of the support was heated in an oxidising ambient, such as air, at a temperature within the range of 400 to 1000°C in
10 order to remove the hydroxyl groups on the support. After the oxidising treatment, the oxygen was purged by nitrogen or argon gas flushing. At normal pressure and at a temperature ranging from 100 to 400°C, a known amount of the reagent, in the example 0.5 to 4.0 ml of chromyl chloride,
15 was then injected into a stream of nitrogen gas conducted through the support, the reagent vapours reacting with the hydroxyl groups of the support. Unreacted reagent vapour was withdrawn from the reactor.
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25 The surfaces of the support particles used in heterogeneous catalysts are structurally inhomogeneous. As far as zeolites are concerned, the crystalline structure of the material is also complex containing, e.g., pore openings having diameters ranging from 0.3 to 0.7 nm. As a consequence of the above characteristics, the surfaces of the support materials
30 are chemically inhomogeneous containing numerous binding sites of different valencies for new atoms or molecules contacted with the surface of the support. It is difficult to control the binding of the metals or metal compounds used as reagents when following any of the conventional practices
35 described above in references [5] to [10].

The conventional processes also present difficulties in achieving homogeneous dispersion of the metals or the metal

compounds on the support surfaces.

The present invention aims at eliminating the drawbacks of the prior art and at providing an entirely novel technical solution for gas phase preparation of heterogeneous catalysts.

The invention is based on the concept of bringing the catalyst reagent in vapour state to the reaction chamber in an amount that at least corresponds to the amount of binding sites on the support surface. It is preferred to use an excess of reagent in relation to the available surface binding sites. The temperature of the support is kept higher than the condensation temperature of the vapour and sufficiently high for the active species or its precursor to be chemisorbed on the surface of the support. In other words, the process aims at providing the thermal activation energy needed for the formation of bonds between the active species or its precursor and the surface of the support.

In particular, the process according to the invention is mainly characterised by what is stated in the characterising part of claim 1.

The apparatus for preparing the heterogeneous catalyst according to the invention is characterised by what is stated in the characterising part of claim 15.

Surprisingly, it transpires that under the above-mentioned conditions a heterogeneous catalyst is obtained, whose activity even at small amounts of the active species is high.

We do not yet fully understand all the reasons underlying this phenomenon and we do not wish to limit the invention to any particular theory. It does, however, appear possible that, under the conditions of the invention, the binding of the active species to the different binding sites of the surface is determined by the structural geometry of the

also comprise a substance which itself catalyses the desired chemical reaction. These supports are exemplified by the natural or synthetic zeolites. It is to be understood that, within the scope of this application, the term "support" 5 also encompasses inactive supports having a catalytically active species bound to their surface. Thus, for instance, when bimetal catalysts are prepared, the first species may provide the support surface for the second species.

10 The reaction chamber is the space, within which the support and the reagents are contacted.

Chemisorption refers, in general, to a process, in which the gaseous, liquid or dissolved compound is bound or 15 attached to the surface of a solid or liquid substance in such a way that a bond, essentially of a chemical nature, is formed.

20 Physical adsorption (or physisorption) is a process which, in essence, involves the physical adsorption of a substance on the surface of another substance by intermolecular forces known as the van der Waals forces.

Condensation means the liquidification or solidification of 25 vapours and gases by cooling.

The present process comprises three basic stages, including the pre- and posttreatment stages, which are part of the preferred embodiments of the invention, although they are 30 not essential as far as the basic solution of the invention is concerned.

35 The process parameters of the method are the temperatures and the duration of each of the given stages. The selection of process parameters is influenced by the actual support-reactant combination.

In the present invention, all the reagents for the pre-treatment, for the binding of the catalytically active

species and for the posttreatment are routed to the reaction chamber in vapour form typically one at the time. The vapour pressure of the vaporized catalyst reagent is maintained at a sufficiently high level and the duration of its interaction with the surface of the support is sufficiently prolonged that at least an equal amount or, preferably, an excess of the reagent is provided in relation to the binding sites available on the support. In relation to the atom layer or molecular layer filling all of the available surface binding sites, a 1.5- to 1000-fold surplus of the reagent and preferably a 2-to 100-fold surplus is normally used. The monolayer amount of the species can be calculated using, for instance, the BET method on the basis of the surface of the support and the molecular structure of the surface.

In the context of the invention, reaction conditions are sought in which the gas-phase reagent (the active species or its precursor) fills all or essentially all of the binding sites available to provide saturation of the surface at the prevailing temperature.

During the reaction, the temperature should not be allowed to drop below the vaporization temperature of the reagent. Neither must the reagent be allowed to condense on its route to the reaction chamber, but the temperature of the feed piping should be kept close to the reaction temperature.

The reagent and the temperature employed are selected in such a way that the reagent does not decompose and the decomposition products, if any, do not condense.

In a preferred embodiment of the invention, a temperature gradient is formed, increasing from the reagent source towards the reaction chamber.

It is possible experimentally to determine a temperature range, or temperature interval, within which the reaction is most advantageously conducted. The lower limit of the

temperature range is determined by the condensation temperature of the evaporated reagent and the activation energy necessary for establishing the desired surface bond. The condensation temperature is not, by itself, an appropriate lower limit if it is too low to provide the reagent with the energy needed for surpassing the activation threshold.

5 The upper limit is determined by the temperature at which the active species, or its precursor chemisorbed on the support, starts to show a significant rate of desorption from the binding site, i.e. when the equilibrium of the chemisorption-desorption reaction has shifted toward desorption. The reagent is selected such that the activation energy required by the chemisorption is exceeded at a temperature at which desorption is still not significant.

10 In most cases, the activation and desorption energies are not known and, thus, the selection of suitable reactants and temperatures is determined by experimentation.

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20 In the process constituting part of the present invention, the pretreatment, the binding and the posttreatment temperatures of the catalytically active component can differ from each other. However, it is required that limit T_{min} , for each reagent used, be exceeded during each process stage. Sometimes the temperature of the pre-treatment will influence the amount of active species or its precursor bound to the support. This is the case, for example, when chromium is bound to the surface of silica. The binding temperature ($>T_{min}$) might then, in turn, influence the amount of the active species or its precursor chemisorbed to the support. This phenomenon can be illustrated by the preparation of the alumina-supported rhenium and the silica-supported zinc catalysts. As will become evident from the following examples, the temperature is generally kept below 500°C, although this temperature does not represent an absolute upper limit.

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The reaction between the catalyst reagent vapour and the support may be carried out at elevated pressure, ambient

pressure or in a vacuum. In the preferred embodiment of the invention, the process is carried out at a reduced pressure ranging from 0.1 to 100 mbar. The benefit to be gained by using reduced pressure resides in improved purity of the reaction chamber and increased diffusion rate.

The pretreatment and posttreatment stages can, similarly, be carried out at elevated pressure, ambient pressure or reduced pressure.

The reaction time is predominantly affected by the penetration of the vapour molecules into the pores or cavities of the support. The gas diffusion between the support particles constitutes an extremely fast process in comparison to the diffusion towards the inner parts of the pores. The reaction time should be kept long enough to allow the vapour containing the active component to interact with the binding sites of the support and to provide the desired surface saturation. In the experiments conducted, the results have indicated that the reaction time can be selected in the range from 0.5 to 25 hours. Usually 1 to 4 hours is enough for achieving the desired goal.

In practice, the above-mentioned process parameters must be determined experimentally, since it is practically impossible to determine the exact binding properties between the support and the gas molecules. Almost every bound species affects and changes the surface areas immediately adjacent, which gives cause to changes in the surface potential.

Summarising, the different stages of the process can be characterised as follows:

Pretreatment:

As mentioned above, the basic structure of the support materials of the heterogeneous catalyst are different. Thus, the atoms or molecules of the vapour-phase catalytically active substance may, under the same ambient conditions,

react in very different ways with different supports. The pretreatment stage of the support is, therefore, important. The pretreatment aims at providing the desired binding sites for the catalytically active component that is to be bound to the support.

The pretreatment can be effected by heating the support or by treating it chemically or as a combination of these two operations.

The heat treatment can, for instance, comprise increasing the temperature of the support to the same temperature as used for binding the active component. In this case, it is preferable for temperature to be increased at a steady rate over a given period of time.

The support may also be heated for some time, normally for between 1 min and 100 hours, preferably from between about 2 and 30 hours, at a selected pretreatment temperature that is either higher, as high as or lower than the temperature used for binding the component. The suitable temperature depends on the support, on the catalytically active species to be bound, and on the binding temperature selected. A pretreatment temperature higher than the reaction temperature leads, with a high probability, to a stable and reproducible surface situation in the actual reaction stage. Too high a pretreatment temperature may, however, change the desired surface structure of the support. At too low a temperature, it is not possible efficiently to remove undesired molecules of substances physically adsorbed on the surface.

In the chemical treatment of the support, the support can be treated with a chemical substance, such as water (steam), for forming hydroxyl groups on the surface, or alternatively, with a dehydrating agent for removing hydroxyl groups. The support can also be treated with a volatile metal compound, such as a magnesium or titanium compound.

It is also possible to combine the above-mentioned heat treatment and the chemical treatment, the support being

heated to or maintained at the desired temperature, while subsequently contacting the surface with a chemical substance, such as steam. Thus, according to one embodiment of the invention, the support is pretreated at a high 5 temperature for removing adsorbed water. After this, the temperature of the support may possibly be changed and steam allowed to interact with the surface, on which chemisorption of new hydroxyl molecules can then proceed. The actual reaction is thus finally carried out either at the same or 10 at another temperature.

The binding of the active species:

The surface-activated support is contacted and interacts 15 with vapour containing the component (i.e. species of precursor) that is to be bound. The component is bound to the surface by selectively filling the available surface binding sites. As mentioned above, the temperature and the duration 20 of the process are determined experimentally for each support material, while taking the activation conditions and the characteristics of the vapour containing the binding component into account.

Several different kinds of active species may be bound to 25 the support as an outcome of the process in the invention. In a multi-species catalyst, the binding order may vary, the result being different kinds of catalysts.

Modification of the binding surrounding of the catalytically 30 active species:

In order to optimise the properties of the catalyst, the prepared specimen can, if necessary, be subjected to post-treatment. This may, for instance, comprise a heat treatment 35 in which the catalyst is heated to a desired temperature which generally is at least in excess of the binding temperature. When the degree of oxidation of the active site of the catalyst is to be changed, the heat treatment is carried out in oxidising or reducing conditions.

During the heat treatment the catalyst atoms may be contacted with a vapour, e.g. steam, that modifies the binding surrounding. This modification may be necessary, e.g. when the precursor of the catalytically active species comprises a reagent molecule deposited on the surface of the support, a part of which is to be removed after the binding. Thus, to continue the example, chlorine atoms are often detrimental to the activity of the catalyst and they can be removed by steam or hydrogen sulfide treatment.

In order to modify the properties of the catalyst, a single or several further species may be added by repeating the procedure described above in such a manner that a vapour containing a new species or its precursor is chosen for the actual binding reaction. The stages of the process can be repeated for a desired amount of new species, with the option to conduct heat treatment and/or chemical treatment between the stages.

There are considerable benefits to be gained by the invention. Thus, for example, in the case of chromium-titanium/silica and rhenium/alumina catalysts, the catalysts have been found to be active at lower metal loadings than previously reported in the literature. This would suggest that the metal is more evenly distributed than in the catalysts prepared from solutions. The ability to control the binding of the metal during the preparation is improved. It is easier to bind several metals than from solution. The metal may be bound in the form of different compounds to the same support, with the necessary ligands being readily obtainable. The impurities caused by the reagents are diminished. The temperature of the process may, in some cases, be lowered.

As a product of the process described in the invention, heterogeneous catalysts exhibiting different basic structures may be prepared. The catalysts used in oil refining, the metathesis catalysts and the polymerisation catalysts may be

mentioned by way of example. In the following discussion, the main groups of catalysts are represented by zeolite-supported zinc, alumina-supported rhenium and silica-supported chromium. However, it is also possible to prepare other noble metal catalysts and transition metal catalysts.

In the following, the invention will be examined with the aid of a detailed description and working examples. It should be noted that the description relates only to some of the preferred embodiments of the invention. Within the scope of the invention, however, other embodiments are quite as conceivable.

Figure 1 shows in cross-section one possible reactor design for carrying out the process according to the invention.

Figures 2 and 3 depict the binding of Zn on the surface of a zeolite support as a function of the binding temperature.

Figure 4 portrays the influence of support preheating on the binding of chromium from CrO_2Cl_2 to silica.

Figure 5 depicts the binding of chromium to silica as a function of the reaction temperature.

Figure 6 illustrates the activity of a silica-supported chromium catalyst in comparison to a prior art catalyst.

Apparatus used for preparing the catalysts according to the invention

The test reactor used in the working examples comprises a longish reactor body 1 and a reactor chamber 4 fitted within said reactor body. In the reactor chamber, there is a container 5 for the sample 6, i.e. the support material. In the reactor body 1 at the end containing the reactor chamber 4, there is a loading/unloading cover 3 for exchanging the reactor chamber with the sample container 5. In order to seal the reactor body 1 hermetically, the cover 3 is provided with suitable sealings, such as annular sealing rings.

Heating elements 7, 8, 9, are mounted around the reactor body 1 for providing the necessary temperature in the different parts of the reactor. The heating elements 7, 8, 9 can, for instance, consist of heat resistances.

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A protecting gas, typically nitrogen and/or argon, is fed into the reactor chamber 4 through a feed conduit 10, the gas atmosphere within the reactor body 1 being controlled by a regulator mounted on the feed conduit 10. In order to provide reduced pressure, the reactor chamber 4 can be connected to a vacuum pump 24 by means of a suction pipe 25. The vacuum pump is also connected to the gas space defined by the reactor body 1 via a vacuum pipe 11. The vacuum pump used may be of a conventional membrane or piston pump type. If necessary, a liquid nitrogen trap should be fitted between the pump 24 and the evacuated spaces for collecting condensing fumes.

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There are two feed conduits 12 and 13 fitted within the reactor chamber 4. It is possible to feed vaporized catalyst reagent via these pipes to the reactor chamber 4. The feed pipe 12 is connected to a gas source, the reagent transport gas being fed into the pipe at the point indicated with an arrow. The gas flow is controlled by a regulator 17. The vessel 16, which is also referred to in the following as the hot source, is used for reagents that are solid or liquid at ambient temperature. The reagent is vaporized by heating it to the desired vaporizing temperature by means of heaters 8 and 9. By adjusting the gas flow with the aid of the regulator 17, it is possible to control the flow of the reagent vapour generated in the hot source to the reaction chamber 4.

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The second feed piping 13 is connected to two gas sources 14 and 15 used for feeding reagents that are vaporous or liquid at ambient temperature. Pressurised reagent is fed from the gas source 14, which typically is a gas cylinder, via a valve 18 to the feed pipe 13. The gas source 15 is used for

reagents having a rather low vapour pressure in comparison to the reaction chamber. These reagents are normally liquid at room temperature. The regulators, i.e. for instance the valves 19, 20, 21, control the flow of the reagents from the gas source 15 to the feed pipe 13. The feed pipe 13 is connected before the regulator 21 to the transport gas source at the point indicated by an arrow (pipe section 26). The transport gases used for feeding the reagents from gas sources 14 and 15 preferably comprise inert gases, such as nitrogen and/or argon.

The reagents used for the chemical pretreatment are fed from sources 14, 15 or 16, respectively.

The apparatus used in the working examples further includes a mass spectrometer 22 for analysing volatile reaction products from samples withdrawn through the regulator 27. The mass spectrometer also comprises a two-part pump arrangement 23 including a prepump and a high pressure pump.

The apparatus is used as follows:

A suitable amount of a support material 6 is placed in the sample container 5 in the reaction chamber 4. In the working examples, the scale of the operation has been small, and usually samples weighing in a range from 3 to 10 g have been used. A liquid or solid reagent is placed in container 16. The reactor body 1 and the reaction chamber 4 are subsequently evacuated by feeding protecting gas via the feed conduit 10 and the feeding pipe 13 at a low flow rate (controlled by regulator means 28 and 21), while providing a reduced pressure in the reaction chamber 5 by means of vacuum source 24. Normally, the goal is to achieve a pressure amounting to a few millibars, e.g. 3 to 10 mbar.

If necessary, the support 6 is then pretreated. As mentioned above, the heat treatment may be carried out using various heating times and temperatures; the temperature is normally in the range from about 200 to about 500°C, whilst the

heating time is about 10 to 30 hours. During this period of time the reagent in container 16 is not normally heated.

During chemical pretreatment or blocking, the reactants are fed from sources 14, 15 or 16. Thus, e.g. steam is conducted from source 15 by routing the protecting/transport gas flow via source 15 (valve 21 is closed and valves 20 and 19) are opened.

Before initiating the reaction, the temperature of the reagent in source 15 is increased to the desired level by the heater 9. Use of the heater 8 enables an increasing temperature gradient to be established between the hot source 16 and the reactor chamber 4, the temperature of the reactor chamber 4 being higher than the temperature of the hot source 16.

The regulator 17 is next opened and reactant vapour is fed by the transport gas into the reactor chamber 4. The reactant is metered at a dosage larger than that required by the number of surface binding sites.

The gaseous reagent diffuses into the support 6 in the sample container 5 and the surplus gas is withdrawn through channel 25 by means of the vacuum pump 24. A part of the gas stream flowing from the reaction chamber 4 is conducted via valve 27 to the mass spectrometer for analysis of its composition.

When using gaseous reagents, these are fed from gas sources 14 and 15. The reagents that are gaseous at room temperature are preferably fed from a gas cylinder 14, and liquid reagents from a liquid container 15. The reagents flowing through the feed pipe 13 are heated to the desired temperature by heaters 8 and 9. The temperature of the feed pipe is always kept higher than the condensation temperature of the reagents.

The process is continued until the desired surface reaction has reached a state of saturation. The supply of the reagent

is then cut off. The temperature and the pressure are returned to normal (STP). If necessary, the catalyst is removed from the apparatus in an atmosphere of protecting gas.

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Preparation of the catalysts:

1. Supports and reagents

10 The zeolite support was comprised of a mixture of a HZSM-5-type zeolite and silica.

15 The zeolite was prepared as follows: 2300 g of tetra-propyl-ammonium bromide, 100 g of sodium aluminate, 2760 g of silica gel (Ludox), 114 g of sodium hydroxide and 18500 g of water were transferred into an autoclave, the temperature was increased to 165°C, and the chemicals were allowed to react for 144 h. The mixture was then rapidly cooled to ambient temperature, after which the product was recovered and washed with 150 l water. The product obtained was dried for 24 h at 20 120°C and calcined for 15 h at 540°C. The sodium-containing zeolite was ion exchanged with a 5 % w/w ammonium nitrate solution. The ion exchanged product was dried for 24 h at 120°C. Next, the zeolite was calcined for 15 h at 540°C.

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When the HZSM-5 zeolite (Si/Al = 40) was ready, 100 g of the zeolite, 100 ml of silica gel (Ludox AS-40) and 10 ml of water were mixed in a mortar, moulded into cakes, dried for 12 h at 115°C, powdered and calcined for 2 h at 540°C.

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The support materials, silica and the γ-aluminium oxide were of commercial quality.

35

The most important data on the support materials are given in Table 1:

Table 1. The properties of the support materials

		H-ZSM-5	Silica	$\gamma\text{-Al}_2\text{O}_3$
5	Particle size [μm]	149-350	53-180	500-1000
	BET Surface [m^2/g]	360	280-330	200
	Pore size [nm] (diameter)	0,55	20	
10	Number of molecules/g	10^{22}	10^{22}	6×10^{21}
	Number of surface molecules/g	2.5×10^{21}	2×10^{21}	1.6×10^{21}
15				

The following reagents were used: metallic zinc, zinc chloride (ZnCl_2), chromium chloride (CrO_2Cl_2), rhenium heptoxide (Re_2O_7), aluminium chloride (AlCl_3), titanium chloride (TiCl_4) and magnesium dipivaloyl-methane [$\text{Mg}(\text{thd})_2$]. The materials were of commercial grade, except for the last one, which was synthesized as described in the publication Hammon, G.S. et al., Inorg Chem 2 (1963), p. 73. The surface of the metallic zinc was treated with hydrochloric acid in order to remove the surface layer before use. Otherwise, the reagents were not pretreated.

2. Analysis

The amounts of elements bound to the supports were determined by means of atomic absorption spectrometry (Al, Ti, Cr, Zn), fluorescence spectroscopy (Zn), polarimetric titration (Cl) or neutron activation analysis (Re). X-ray induced photo-electron spectroscopy (XPS or ESCA) and X-ray diffraction analysis (XRD) were employed for evaluation of the metals on the surface of the catalyst.

Example 1:

The preparation of a zinc/zeolite catalyst

This example illustrates the binding of a metal in elemental state to the surface of the support. Further, the impact of the reaction temperature on the amount of metal bound to the surface is considered in the example.

The zinc/zeolite catalyst is used in oil refining, e.g., for catalysing the conversion of butane to aromatic compounds.

Several catalysts were prepared by binding zinc to the surface of zeolites. The support material lot weighing 2 to 10 g was placed in a sample vessel of a reaction chamber where it was heat treated at 430 to 465°C in a nitrogen stream of 2 to 5 mbar pressure. The pretreatment time was 2 to 24 h.

Metallic zinc placed in a heated source was heated to 430°C and the zinc vapour was routed to the reaction chamber. During each test the temperature of the reaction chamber was maintained above 430°C in order to prevent the condensation of zinc onto the zeolite surface. The zinc vapour was reacted with the zeolite for 1 to 4 h.

The Zn concentrations in the prepared catalysts were between 0.03 and 10 % w/w.

Some of the catalysts thus obtained were subsequently treated with sulphur. Elemental sulphur was placed in the hot source and sulphurous fumes evaporated from it were reacted with the Zn/zeolite catalyst at 465°C.

The binding of Zn as a function of the reaction temperature is depicted in Figure 2. The Figure shows only the results obtained after 2 hours' preheating. Extension of the pre-heating period to 24 hours did not increase the binding of zinc to any larger extent. The logarithm of the ratio of Zn atoms to SiO₂+Al₂O₃ atoms was calculated for Figure 2. The

Example 3

The activity of the zinc/zeolite catalysts

- 5 The activity of the zeolite-supported zinc catalysts was evaluated by testing the catalysts for the conversion of n-butane into aromates and for aromatic selectivity. The test were carried out in a microreactor at ambient pressure and at temperatures ranging from 450 to 500°C. The quantity of the catalyst batch loaded in the reactor was 5.0 g and the feed rate of n-butane into the reactor was 5 g/h. The reaction was monitored with the help of gas chromatography, a sample being taken after each five hours' run at 450°C constant temperature.
- 10 15 Out of the zeolite-supported zinc catalysts prepared according to the invention, three catalyst were subjected to analysis runs. Two of the catalysts had been prepared at 430°C and the third one at 470°C. The catalysts contained 0.66, 0.65 and 1.07 % w/w, respectively, of zinc. The support of the first catalyst had been pretreated for 2 hours at 500°C before the binding reaction. Reference catalysts were prepared by the dry impregnation technique, which involved impregnating 0.5 ml zinc nitrate solution into each g of an H-ZSM5-zeolite/silica support. Said catalysts were dried at 115°C for 12 h, and subsequently calcined at 540°C for 4 hours. The catalysts prepared by impregnation contained 0.15 and 1.4 % w/w, respectively, of zinc.
- 20 25

The test results are shown in Table 2:

Table 2. Butane conversion and aromatic yield

Catalyst	Zn conc. [% w/w]	Butane conversion [% w/w]	Aromatic selectivity [%]	Yield [% w/w]
5				
Present invention				
10	3.1	0.66	41.4	36.0
	3.2	0.65	48.4	40.3
	3.3	1.07	41.8	37.2
15				
Reference				
15	3.4	1.40	30.6	37.2
	3.5	1.41	31.4	39.2
	3.6	0.15	44.4	17.3
20				

As is evident from the results, the catalysts produced in accordance with the invention achieve an equal or higher degree of conversion than is obtained with the reference catalyst, while the selectivity to aromatic compounds is at least at an equal level. Both the conversion and the aromatic selectivity are on an industrially applicable level.

Example 4

The preparation of a Re/Al₂O₃ catalyst

30 The Re/alumina combination is a well-known metathesis catalyst which can be used, e.g., for catalysing the disproportionation of propane to ethane and butane. Following to the process outlined for the invention, rhenium was bound to the surface of γ -alumina from rhenium heptoxide, which is a solid substance at ambient temperature.

35 The catalysts were prepared using coarse-grain alumina as support. Re₂O₇ (Aldrich Chemicals Co., purity: 99.9 %) was

volatilized by heating it at 160°C. The preheating of the support and the binding of the rhenium were carried out at a 3 mbar nitrogen pressure. The reaction temperature was maintained in the range from 175 to 360°C, an increasing temperature gradient being formed from the hot source towards the reaction chamber. The rhenium heptoxide vapour was contacted with the support for 225 minutes. The rhenium content of the prepared catalyst was determined. Table 3 gives the pretreatment and reaction temperatures.

10

Table 3. Re/ γ -Al₂O₃ catalysts

	Sample no.	Preheating t [h]	Preheating T [°C]	Reaction temperature [°C]	Re [% w/w]
15	4.1	-	-	175	0.3
	4.2	4	220	220	0.1
	4.3	-	-	360	0.04
	4.4	-	-	470	0.65
20	4.5	18	470	475	0.04
	4.6	16	220		
		+ 16	470	470	0.04
	4.7	17	470	360	0.01
	4.8	18	470	220	0.01
25					

The table indicates that a long pretreatment at high temperatures decreases the amount of rhenium binding to the support. The largest amounts of rhenium are bound to the surface of alumina without any heat pretreatment.

30

Test were further carried out to study the influence of a Mg(thd)₂ addition on the support's capability to sorb rhenium. The alumina was first heated at 475°C for 18 hours, then cooled to 240°C and, subsequently, contacted with fumes of Mg(thd)₂ that had been volatilized at a temperature ranging from 75°C to 85°C. In this case, 0.36 % rhenium was bound to the support from rhenium heptoxide. In a reference test, in which no magnesium dipivaloylmethane was

35

used, the rhenium content was 0.12 %. Thus, the amount of Re bound to the support was tripled by the Mg(thd)₂ treatment.

5 The amount of Re bound to the support was rather small in all the tests (< 0.65 %) in comparison to conventional Re metathesis catalysts that can have a Re content of up to 15 %. The activity of the prepared catalysts were assessed on basis of propene conversion. The results indicated that
10 the Re activities on a weight basis were at least as high as those of conventional catalysts, and in several cases much higher. Thus, in the case of the catalyst 4.2, the propene conversion per weight unit of Re was as high as over 6 % and in the case of catalyst 4.8 even exceeded 15 %.

15

Example 5

The preparation of a chromium/silica catalyst

20 Silica-supported chromium is a known Phillips-type polymerisation catalyst. The following example will show in more detail, how the preheating and the reaction temperatures influence the binding of chromium in the process according to the invention.

25 Chromyl chloride, CrO₂Cl₂ was used as a starting compound for the chromium. A silica support (Crosfield Catalysts EP 10 silica gel) the amount of which was 4 to 5.5 g, was pre-heated at 100°C to 360°C in a nitrogen gas atmosphere at a pressure of 3 to 4 mbar for 17 to 20 hours. After the pre-heating the temperature was adjusted to the actual process temperature. Chromyl chloride was evaporated and reacted with the silica at 175, 270 and 365°C temperatures. The reaction time was in excess of 1.5 hours, typically 2.5 hours.
30
35

Table 4 gives the test operating conditions of three Cr catalyst tests:

Table 4. Operating conditions of Cr catalyst tests

Test no.	Preheating T [°C]	Reaction temp. t [h]	CrO ₂ Cl ₂ T [°C]	Time moles/g/run	[min]
5					
5.1	360	20	175	0.2	97
5.2	360	17	175	0.13	150
5.3	100	17	175	0.10	150
10					

The CrO₃ layer completely covered the surface of the silica support and was calculated to contain about 0.16 g chromium per 1 g silica. This corresponds to a molar content of approx. 0.003 mol chromium. The reagent used in the tests exceeded the available binding sites on the support by about 30- to 70-fold.

The preheating temperature determines the number of OH-groups in silica and thus the number of binding sites. The chromyl chloride molecule can bind either to one or two hydroxyl groups releasing one or two molecules of HCl, respectively. The highest chromium concentrations were found after preheating at 270°C. Reaction temperatures for chromyl chloride between 150 and 330°C did not have a major effect on the chromium concentration.

The average Cr concentration as a function of the pretreatment temperature is shown in Figure 5.

Figure 6 shows the influence of the reaction temperature on the binding of chromium. In a similar manner as in Figure 2, the ratio between the catalytically active metal and the support molecules was calculated. The figure also includes an indication of the respective amounts of chromium and chromium oxide covering the silica surface in the form of a monolayer. When the preheating temperature is raised above 480°C, the Cr concentrations were less than 0.02 %,

irrespective of whether the reaction temperatures were 175, 270 or 360°C.

It is worth noting that, according to reference [10], the pretreatment should generally be conducted at a temperature of at least 400°C, preferably at a temperature in the range from 600 to 800°C.

Example 6

Chromium-titanium/silica and chromium-aluminium/silica catalysts

In this example, the binding of a second catalytically active metal on the catalyst prepared in Example 5 was studied in detail. Table 5 contains a summary of the operating conditions of these tests:

Table 5. The test run conditions of Cr-Ti and Cr-Al catalysts

Test no.	Preheating T [°C]	t [h]	Reaction temp. T [°C]	CrO ₂ Cl ₂ mol/g/run	Time [min]
6.1	455	17	270	0.18	150
6.2	360	20	270	0.15	150
6.3	360	17	270	0.29	150
6.4	360	17	270	0.14	150

In test 6.1, following the preheating step, the support was treated with steam for 75 min at 360°C, after which the chromyl chloride was added. When the reaction was completed, a new water vapour (steam) treatment was conducted at 270°C, followed by the introduction of 0.13 mol of titanium chloride (TiCl₄) per unit weight (g) of the support into the same reaction space at the same temperature for 184 minutes. Finally, a further steam treatment was performed for 75 minutes.

In test 6.2, following the pretreatment, the support was reacted with titanium chloride (5 mmol per g of support) at 270°C for 8.3 min. A water vapour treatment was performed for 15 minutes at the same temperature prior to the introduction of chromyl chloride into the reaction chamber.

5 In test 6.3, a Cr-containing silica catalyst was prepared as described in Example 5 above. The product thus prepared was reacted with titanium chloride at 270°C for 8.3 min. The 10 amount of titanium chloride used corresponded to 9.5 mmol Ti/g of support.

15 In test 6.4, following the pretreatment, the support was first reacted with aluminium chloride ($AlCl_3$) at 270°C for 150 minutes. The amount of aluminium corresponded to 2.4 mmol Al per unit weight (g) of the support. Steam was then introduced into the reactor chamber for 75 minutes. The chromyl chloride was added as explained in Example 5.

20 The catalysts prepared contained 0.016 to 0.47 % w/w chromium, 0.32 to 6.2 % w/w titanium and 0.49 % w/w aluminium.

Example 7

25 The catalyst activity of Cr/silica-based catalysts

The catalysts prepared according to Examples 5 and 6 were fluidized in dry air and heated first to 200 to 250°C, at which temperature they were held for 4 h, after which 30 they were finally activated by calcination at an elevated temperature (580 to 780°C) for about 5 h. The calcined material was cooled to 300°C and the air atmosphere was replaced by an oxygen-free nitrogen atmosphere.

35 The catalysts thus treated were used in the polymerization of ethane. The reaction temperature was 105°C and the total pressure 4000 kPa. The hydrocarbon diluent in the polymerization process was isobutane. The results are shown in Table 5, below.

Table 5. Activities of Cr and Ti containing catalysts in polymerization of ethene.

5	Elemental contents				Activation temp [°C]	Activity (gPE/gcat*h)
	Cr	Ti	Al	Cl [%]		
10	5.1	1.4		0.32	570	1400
	5.2	1.5		<0.01	780	1220
	5.3	0.012		0.01	780	200
	6.1	0.47	6.2		730	1600
	6.2	0.016	0.32		690	500
	6.3	0.29	1.3	3.2	790	1000
	6.4	0.026		0.49 3.5	750	475

15

As is evident from the results, the catalysts have a very high activity even in those cases where the metal content is low.

20

The catalyst activity of the catalysts prepared according to the invention have also been compared with the catalyst disclosed in reference [10]. The results are given in Figure 6.

25

In Figure 6, the X-axis indicates the percentage of chromium in the catalysts, and the Y-axis gives the amount of polyethylene formed per weight of the catalyst on an hourly basis. The lines drawn at an angle of 45° to the X-axis indicate the amount of polyethylene formed per hour in relation to the weight of the chromium on the catalyst.

30

The McDaniel and Stricklen catalysts contain about 1 % Cr.

35

Figure 6 shows that, calculated on the basis of PE-conversion per unit catalyst weight, the present Cr catalyst attains almost as high an activity at lower Cr loadings as the best prior art catalysts. At the same time, it should be noted that the known catalysts have been subjected to a separate reducing treatment. From a calculation of the catalyst activity on the basis of the amount of chromium, it appears

that the catalysts prepared according to the invention are considerably more active than the prior art catalysts. The addition of titanium increases the activity of Cr+Ti catalysts. Since the catalysts is retained in the product after the reaction, a decrease in the amount of Cr will provide a valuable additional benefit for catalysts prepared according to the invention.

Claims:

1.. A process for preparing a heterogeneous catalyst having at least one catalytically active species bound to the surface of a support material, said process comprising the steps of

- 5 - optionally pretreating the surface of the support,
- vaporizing a catalyst reagent containing the catalytically active species or its precursor,
- routing the vapour into a reaction chamber where it is brought to interact with the support material, the support being kept at a higher temperature than the condensation temperature of the vapour,
- 10 - removing the catalyst reagent not bound to the support, and subsequently
- if necessary, posttreating the species bound to the support in order to convert it into a catalytically active form,

c h a r a c t e r i z e d b y

- 20 - maintaining the vapour pressure of the vaporized catalyst reagent in the reaction chamber at a sufficiently high level and the duration of interaction with the support over a sufficiently long period as to provide at least an equal amount of catalyst reagent in relation to the number of available binding sites on the support, and
- 25 - maintaining the temperature of the support at a sufficiently high level to attain chemisorption of the catalytically active species or its precursor to the binding sites of the support.

30 2. The process as claimed in claim 1, c h a r a c t -
e r i z e d b y providing an excess of the catalytic reagent
in relation to the available binding sites of the support.

35 3. The process as claimed in claim 1, c h a r a c t e r -
i z e d b y continuing the interaction between the support .

and the catalytic reagent until at least an essential part of the surface binding sites has been occupied.

4. The process as claimed in any one of claims 1 to 3,

5 characterized by maintaining the temperature below the temperature at which the catalytically active species begins essentially to desorb from the support.

5. The process as claimed in any one of claims 1 to 4,

10 characterized by evaporating the catalyst reagent in a separate space and by forming an increasing temperature gradient between said space and the reaction chamber.

15 6. The process as claimed in any one of claims 1 to 5, characterized by subjecting the support to a pretreatment by heat.

20 7. The process as claimed in claim 6, characterized by subjecting the support to pretreatment not only by heat but also by chemical processing, e.g. with steam or a dehydrating agent.

25 8. The process as claimed in claim 6, characterized by carrying out the pretreatment of the support and the actual reaction in the same reaction chamber.

30 9. The process as claimed in claim 1, characterized by carrying out the actual reaction at reduced pressure, typically at a pressure in the range of 0.1 to 100 mbar.

35 10. The process as claimed in claim 1, characterized by modifying the oxidation state of the catalytically active site by heat treatment in oxidising or reducing conditions.

40 11. The process as claimed in claim 1, characterized by posttreating the combination consisting of the catalytically active species and the support by contacting

said combination with a vapour that modifies the binding surrounding of the catalyst atoms.

12. The process as claimed in claim 11, characterized by using water steam as said vapour.

13. The process as claimed in any of the preceding claims, characterized by repeating the process steps at least once for at least one additional catalytically active compound.

14. The process as claimed in any of the preceding claims, characterized by maintaining the temperature during each process step higher than the condensation temperature of each catalytically active compound used.

15. Apparatus for preparing a heterogeneous catalyst comprising at least one catalytically active compound and a support, said apparatus comprising

- a reactor body (1),
- a gas tight reaction chamber (4) fitted within the reactor body (1) for holding the support material (6),
- heaters (7, 8, 9) placed around the reactor body (1) for achieving the desired temperature in the reactor body (1) and in the reaction chamber (4),
- feed (12, 13) and outlet (25) piping connected to the reaction chamber (4) for achieving a protective gas atmosphere inside the reaction chamber,
- gaseous reagent sources (14, 15, 16) connected to the reaction chamber (4) for feeding the catalytically active compound to the reaction chamber space (4), and
- means for withdrawing unreacted gaseous reagent surplus,

characterized in that

- the gas sources (14, 15, 16) are connected to the inert gas feed piping (12, 13) and
- the feed piping (12, 13) is at least partially placed within the reactor body (1) such that the material

flowing in the pipes can be heated to the desired reaction temperature by the heaters (7, 8, 9).

16. The apparatus as claimed in claim 15, characterized in that the heaters (7, 8, 9) are adjusted to form an increasing temperature gradient in the direction of reagent feed.
17. The apparatus as claimed in claim 15, characterized in that the means for withdrawing the unreacted reagent comprises the outlet pipe (25) of the inert gas.
18. The apparatus as claimed in claim 15, characterized in that at least one gas source comprises an open vessel (16) fitted within a feed pipe (12) in which a starting compound in the solid state can be placed and from which the starting compound can be vaporized by means of a heater (9).
19. The apparatus as claimed in claim 15, characterized in that at least one gas source comprises a liquid starting compound source (14).
20. The apparatus as claimed in claim 15, characterized in that at least one gas source comprises a gaseous starting compound source (15).

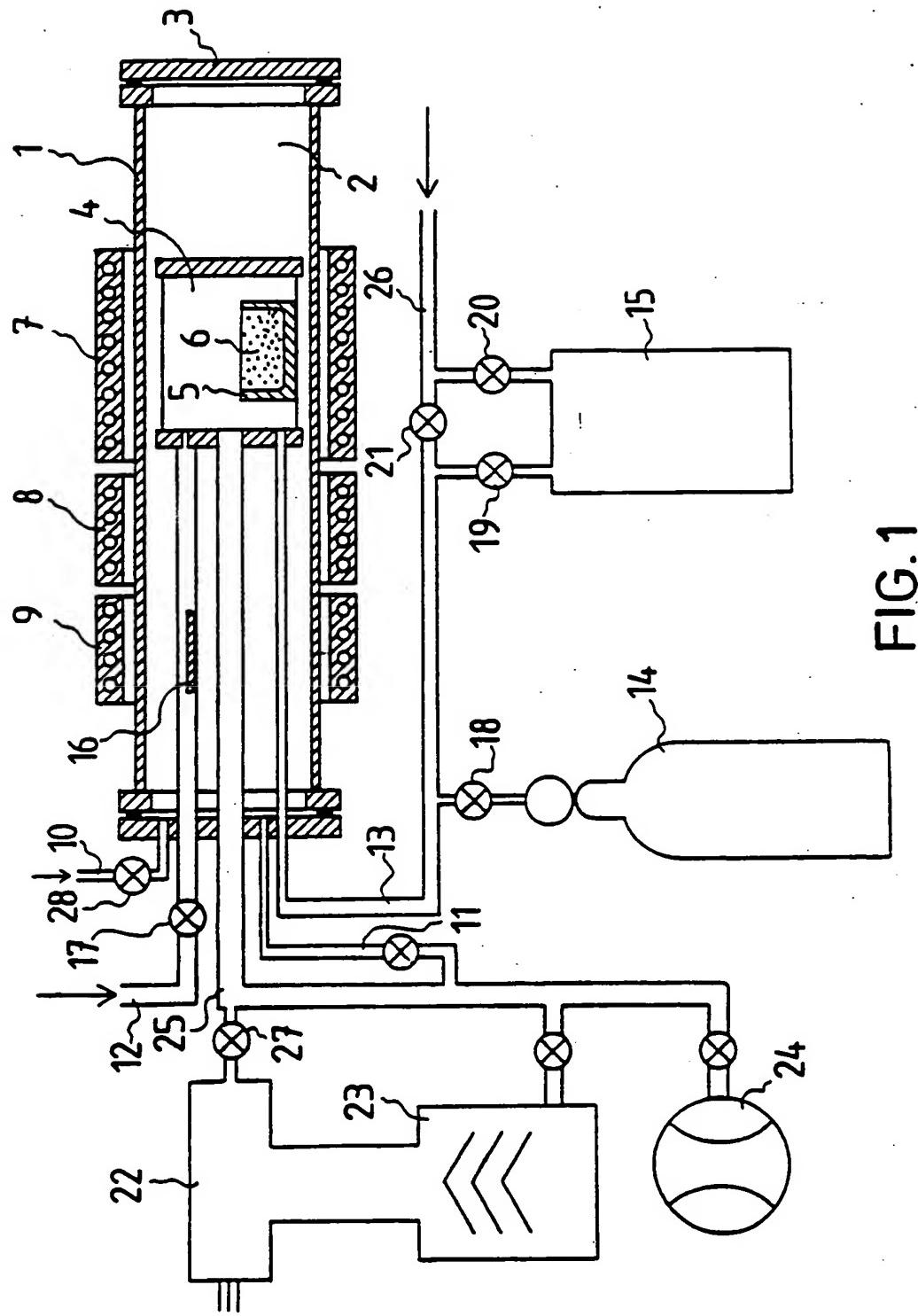


FIG. 1

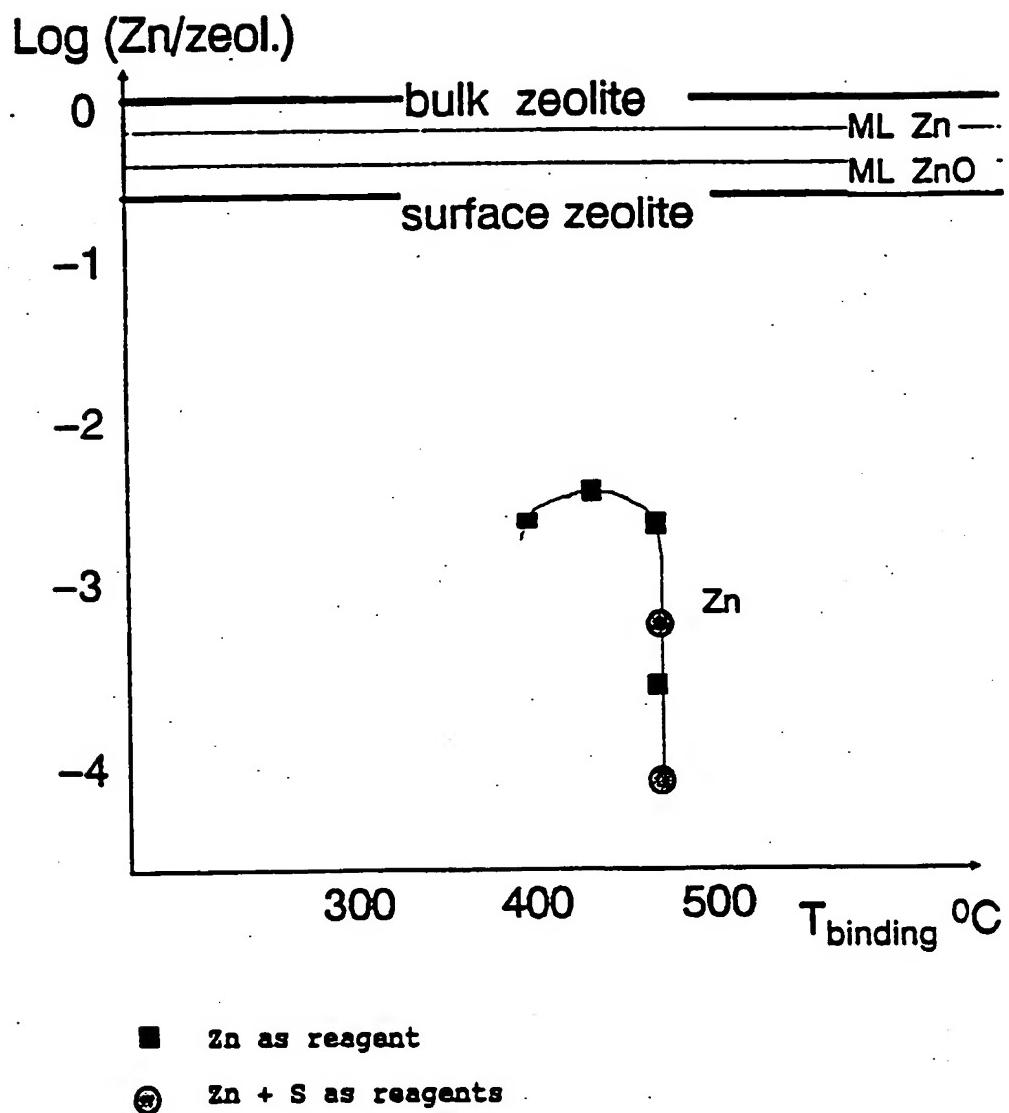
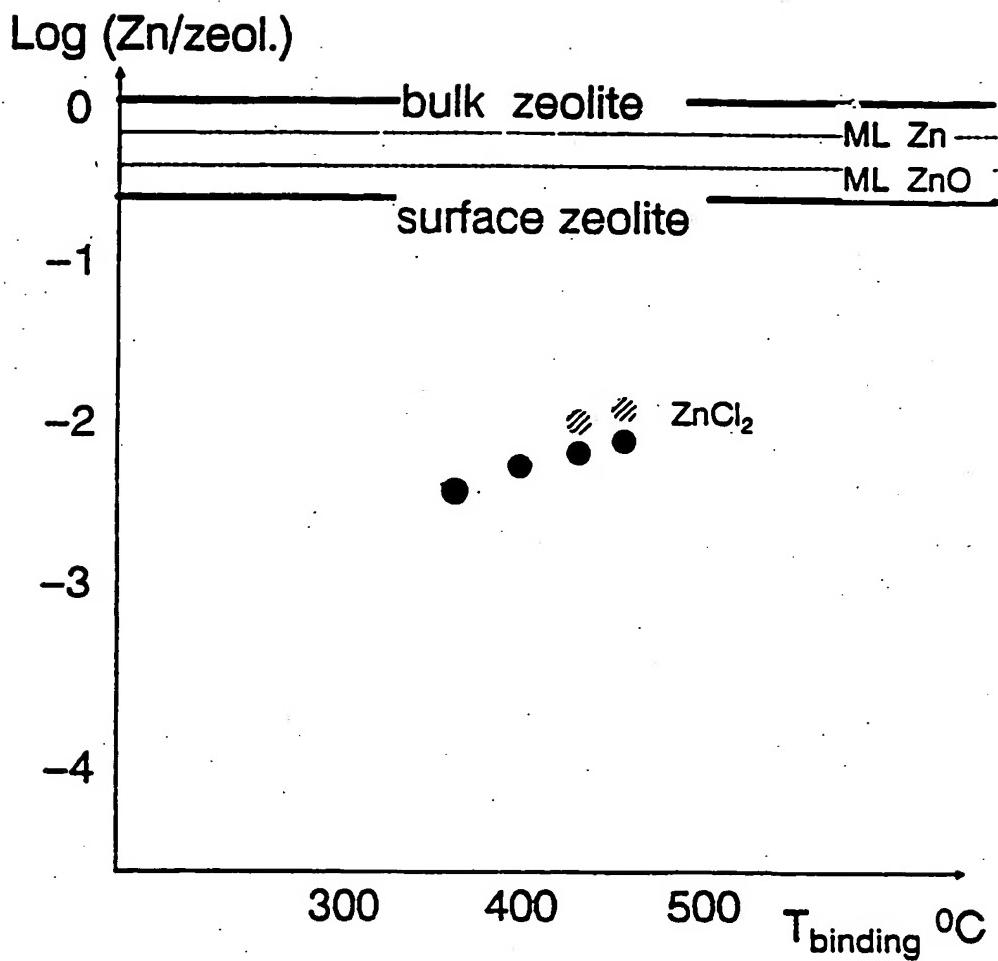


Figure 2. The binding of Zn as a function of the reaction temperature



- No preheating of the support
- ◎ Preheating for 16 to 24 h at reaction temperature

Figure 3. The binding of Zn from ZnCl₂ as a function of the reaction temperature

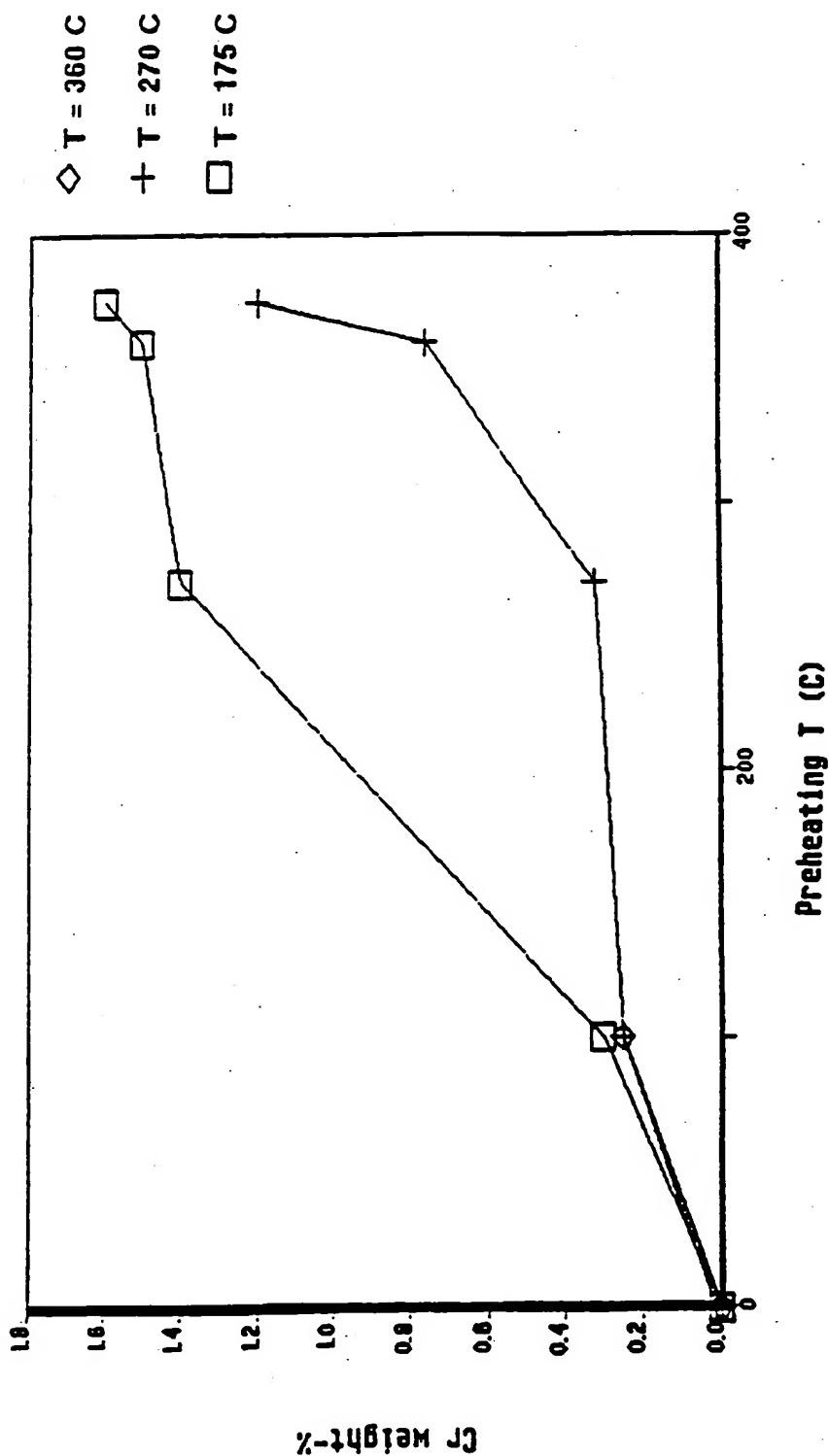


Figure 4. The effect of preheating on Cr binding from CrO_2Cl_2 to silica. The reaction was performed at three temperatures ($T = 175, 270$ and 360°C)

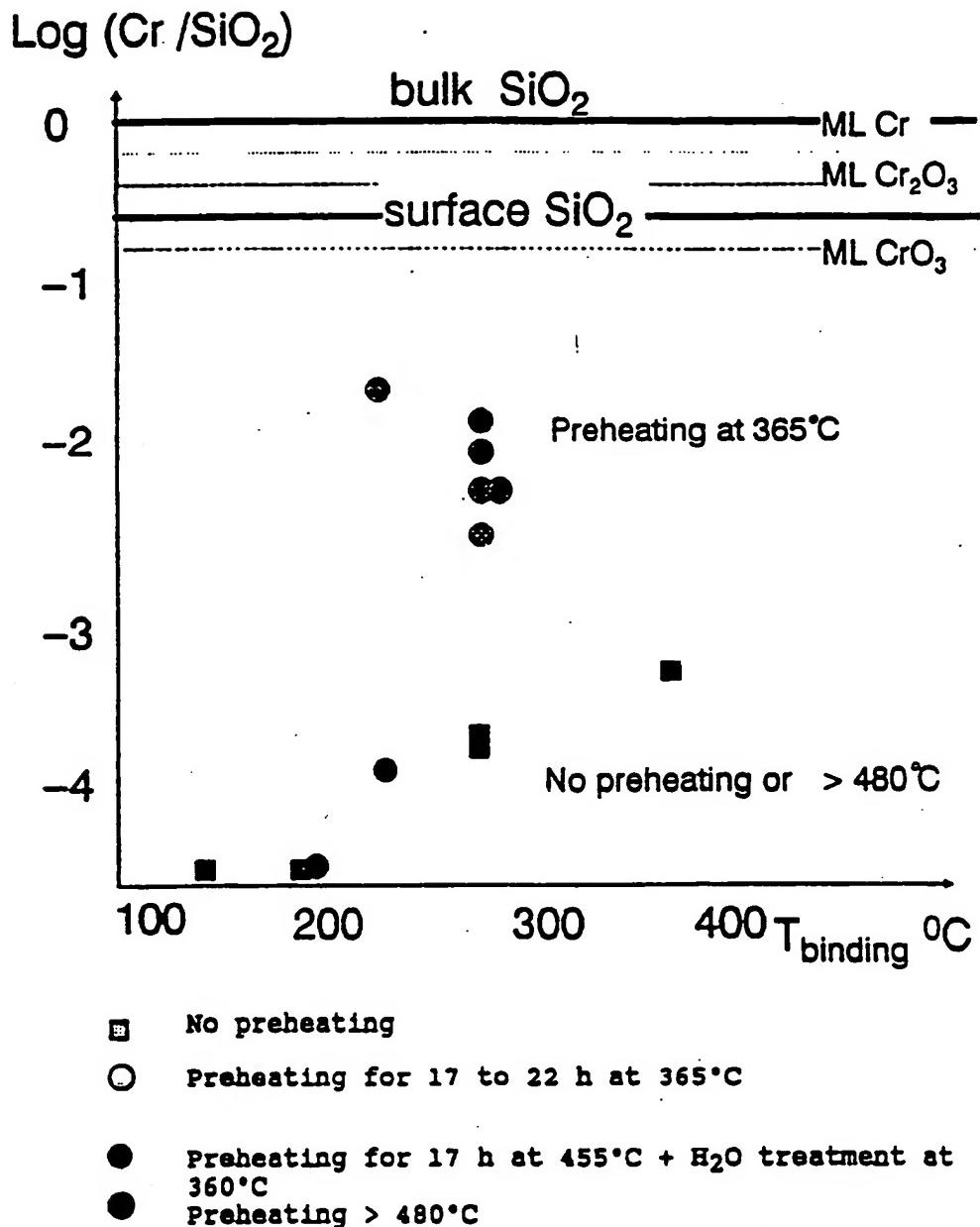
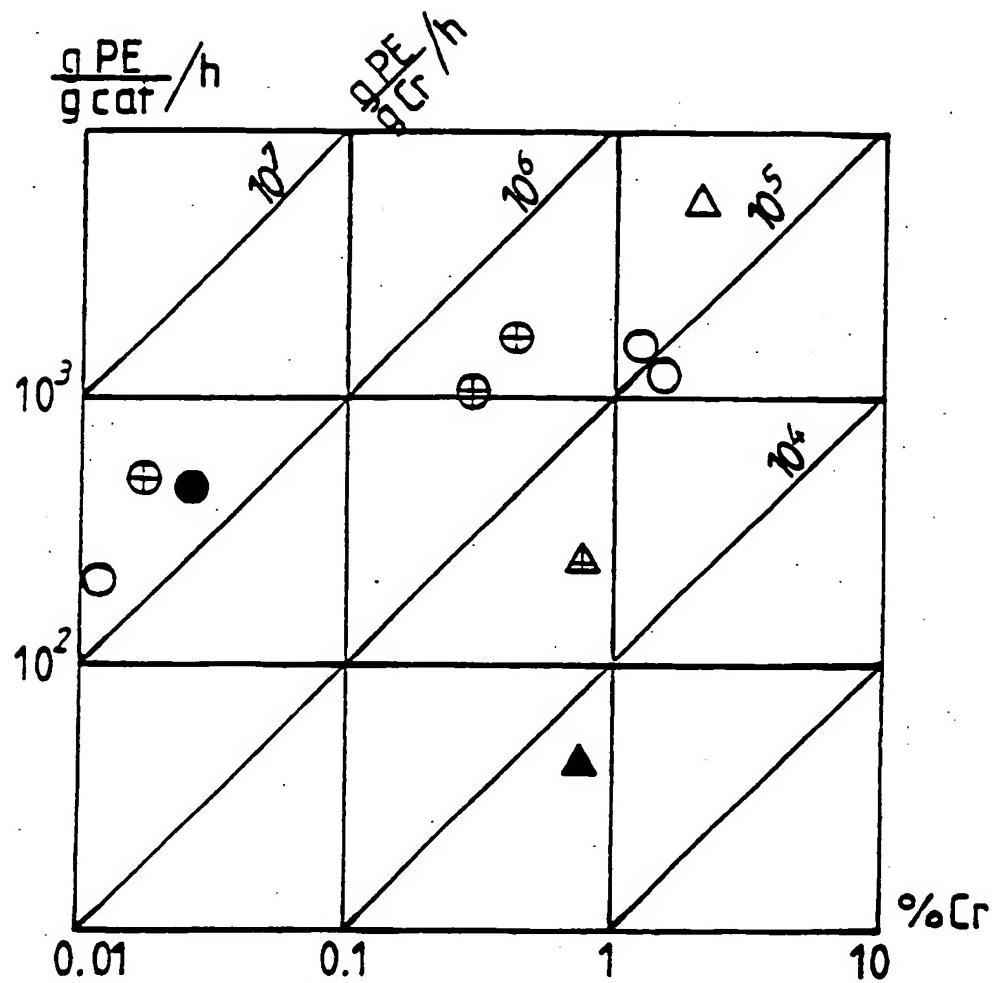


Figure 5. The binding of Cr to silica as a function of the reaction temperature



In accordance with the invention

- O Cr
- ⊕ Cr + Ti
- Cr + Al

Phillips

- △ Cr CO
- ▲ Cr + TE(AL)
- ▲ Cr + TE(B)

FIG.6

INTERNATIONAL SEARCH REPORT

International Application No. PCT/FI 91/00017

L. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all)⁶

According to International Patent Classification (IPC) or to both National Classification and IPC

IPCS: B 01 J 37/02, 37/10

II. FIELDS SEARCHED

Minimum Documentation Searched⁷

Classification System	Classification Symbols
IPCS	B 01 J

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in Fields Searched⁸

SE,DK,FI,NO classes as above

III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹

Category	Citation of Document ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	EP, A2, 0135954 (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.) 3 April 1985, see page 2, line 1 - line 16; page 7, line 13 - page 10, line 9; page 15, line 6 - line 17	1,6,9
Y	--	1,5- 12
X	DE, A1, 2836892 (INSTITUT CHIMITSCHESKOJ FISIKI AKADEMII NAUK SSSR) 27 March 1980, see page 9, line 26 - page 11, line 8 example 1	1,5,6,8- 10
Y	US, A, 4380616 (FRED L. VANCE, JR., ET AL) 19 April 1983, see claim 2 example 1 A	1,9, 10
	--	

* Special categories of cited documents:¹⁰

"A" document defining the general state of the art which is not considered to be of particular relevance

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"C" document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

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"E" document published prior to the International filing date but later than the priority date claimed

"F" later document published after the International filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"G" document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"H" document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"I" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search

22nd March 1991

Date of Mailing of this International Search Report

1991-04-16

International Searching Authority

Signature of Authorized Officer

Ingrid Grundfelt

SWEDISH PATENT OFFICE

Form PCT/ISA/210 (second sheet) (January 1985)

III DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
Y	US, A, 4439543 (MAX P. McDANIEL ET AL) 27 March 1984, see column 2, line 18 - line 25; claims 1,5-7,9,10 example 1 --	1,6-8, 10
Y	EP, A2, 0002272 (PHILLIPS PETROLEUM COMPANY) 13 June 1979, see claims 1,5 --	1,10- 12
Y	FR, A1, 2351703 (JOHNSON MATTHEY & CO., LTD.) 16 December 1977, see example 1	1,5,6,9
A	--	15-20
A	Patent Abstracts of Japan, Vol 12, No 11, C468, abstract of JP 62-168550, publ 1987-07-24 (MITSUBISHI HEAVY IND LTD) -----	15-20

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.PCT/FI 91/00017**

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the Swedish Patent Office EDP file no. 91-02-28
The Swedish Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

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US-A- 4380616	83-04-19		NONE	
US-A- 4439543	84-03-27		US-A- 4503201	85-03-05
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FR-A1- 2351703	77-12-16		BE-A- 854718 CH-A- 622439 DE-A- 2722771 GB-A- 1578123 JP-A- 53001192 NL-A- 7705481	77-09-16 81-04-15 77-12-08 80-11-05 78-01-07 77-11-23